

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.762.36:542.6:546.6

NANOSIZE SINTERING ADDITIVE BASED ON B_2O_3 FOR OBTAINING CERAMIC FROM ALUMINUM-MAGNESIUM SPINEL

S. K. Evstrop'ev,^{1,2} A. N. Smirnov,¹ and V. V. Sharypin¹Translated from *Steklo i Keramika*, No. 7, pp. 16–20, July, 2014.

The results of an investigation of the effect of B_2O_3 as a sintering additive at the initial stages of the formation of optical ceramic from aluminum-magnesium spinel (AMS) are presented. It is shown that uniform nanosize coatings containing the sintering additive B_2O_3 can be obtained on the surface of AMS particles by the liquid method, which significantly accelerates the subsequent sintering of AMS particles.

Key words: aluminum-magnesium spinel, ceramic, coating, sintering additive.

It is well known that optical ceramic made from aluminum-magnesium spinel (AMS) is a promising material for multispectral electrooptic systems and structural optics [1, 2]. The principal factors influencing the production of dense AMS ceramic are: the properties of the initial powder, purity, particle size of the initial material, initial density and sintering regime.

One of the most effective technological expedients making it possible to lower the temperature and decrease the duration of the sintering of a ceramic material is to introduce a sintering additive into the batch. To obtain a dense ceramic from AMS it is important to pick a sintering additive and a method of introducing it into the batch. Usually, metal fluorides, specifically, LiF, are used as the sintering additive to obtain the highest density ceramic from AMS [3, 4]. The low solubility of LiF and, correspondingly, the technological difficulty of obtaining a uniform distribution of such a sintering additive in the initial AMS powder make it necessary to consider the possibility of using more promising, forms of an effective sintering additive as an alternative.

In [5] B_2O_3 introduced into AMS powder in amounts 0.05–0.5% (mass fraction) was proposed as an alternative sintering additive. The use of B_2O_3 as a sintering additive made it possible to significantly accelerate sintering and obtain a dense ceramic. To introduce this additive the AMS powder was mixed with a solution of H_3BO_3 in ethanol, dried and comminuted.

Ordinarily, sintering additives are introduced by mechanical mixing of the components of the additive with AMS powder. The drawback of this method is that large nonuniformities are formed in the structure of the material as a result of particles of different sizes being introduced.

The aim of the present work was to investigate the effect of B_2O_3 on an important initial stage of formation of a dense ceramic from AMS. The effect of LiF on the particles of AMS powder during heat-treatment in air at temperatures 900–1600°C was studied for comparison.

SYNTHESIS AND INVESTIGATION PROCEDURE

The initial materials for fabricating ceramic were AMS powder of different degrees of dispersity: sample 1 (AMS-1) consisted of particles of average size 1 μm with specific surface area 17 m^2/g and sample 2 (AMS-2) consisted of nanoparticles of spinel of average size 47 nm with specific surface area 166 m^2/g .

Two different methods were used to add the sintering additive.

Method 1. Weighed portions of boric acid and AMS powder were mixed in ethanol and allowed to stand at room temperature for 1 h, after which the powder was separated from the solution and dried at 80°C for 18 h. This method differs fundamentally from the one used in [5] by the fact that before drying the AMS powder is separated from the solution in order to prevent any possibility of formations with uncontrollable size being formed in AMS because of precipi-

¹ S. I. Vavilov State Optics Institute, St. Petersburg, Russia.

² E-mail: evstropiev@goi.ru.

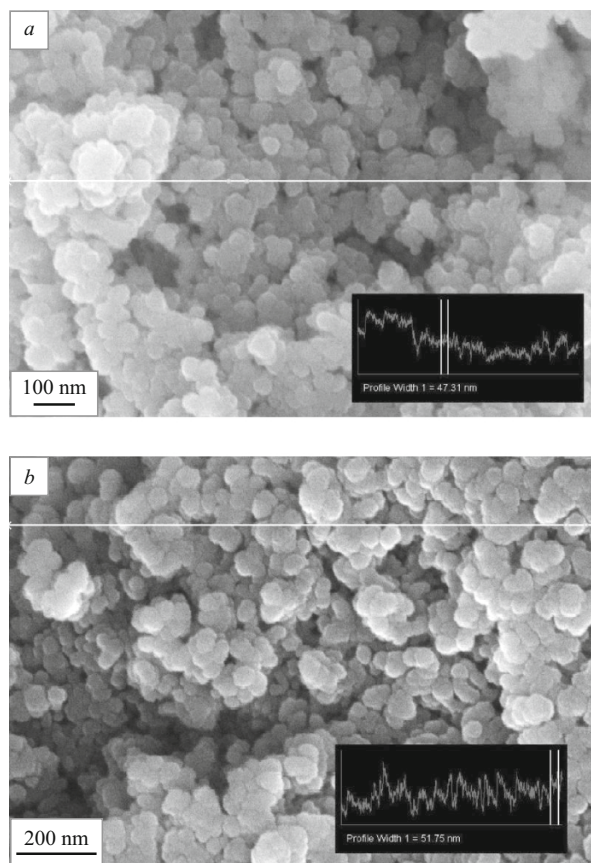


Fig. 1. SEM photograph of the initial aluminum-magnesium spinel AMS-1 powder: *a*) untreated; *b*) treated with an alcohol solution of H_3BO_3 .

tation of the excess boric acid present in the solution. Samples in the form of 20 mm in diameter and 4 mm thick pellets were pressed from the AMS powder obtained. The experimental conditions had a large effect on the density of the samples obtained. It is well known that the presence of a liquid in powdered batch can promote densification of the material during processing [6]. To determine the effect of additions of different liquids on the density of the compacts 10 samples of each of type of liquid were fabricated in the form of pellets and their density after drying and heat-treatment was measured.

Method 2. Porous ceramic samples made from AMS-1 and AMS-2 powders were permeated with an alcohol solution of boric acid. The permeation was accomplished by immersing the samples for 5 min in an alcohol solution of boric acid with different concentrations. Next, the permeated pellets were dried at 80°C for 18 h and sintered at 1300°C for 6 h. Samples in the form of 20 × 4 mm pellets were cold-pressed under pressure 100 MPa and soaked for 5 min. Next, the samples were sintered at temperature 1200°C for 2 h. The sintered AMS-1 and -2 samples acquired relative density 49 and 79%, respectively.

A DRON-2 diffractometer was used to perform x-ray structural analysis using Cu- K_α radiation. The spinel struc-

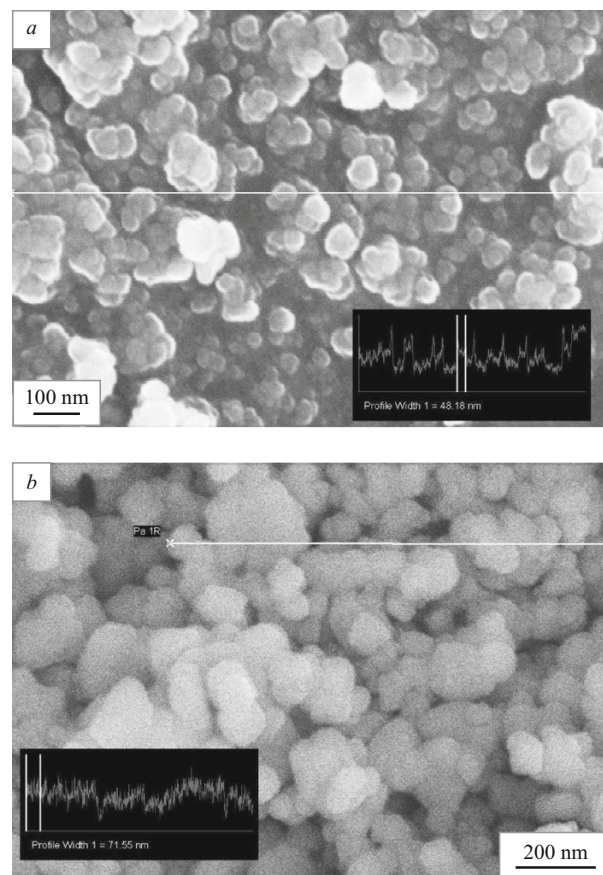


Fig. 2. SEM photograph of AMS-2 powder treated with an alcohol solution of H_3BO_3 and heat-treated for 80 min: *a*) at 900°C; *b*) at 1100°C.

ture was determined on the basis of the (111), (220), (311) and (400) lines. The grain size was found according to the half-width of the instrumental line (311).

A SUPRS 55VP-25-78 scanning electron microscope (SEM) was used to study the surface morphology of the particles of the AMS samples.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the investigations of the surface morphology of the particles of untreated AMS-2 powder as well as AMS-2 powder permeated with an alcohol solution of boric acid are presented in Fig. 1*a* and *b*, respectively. The initial powder (Fig. 1*a*) consists of uniform particles with average size 47 nm. The average size of the particles treated with a boric acid solution was 52 nm (Fig. 1*b*). The deposition of a coating did not change much the morphological features of the surface structure of the particles in the sample, but a uniform 2 – 3 nm thick layer of boric acid was formed on the surface of the AMS particles by the permeation method.

SEM photographs of AMS-2 samples treated at high temperature are displayed in Fig. 2. The surface of the particles is coated with B_2O_3 as a result of decomposition of boric

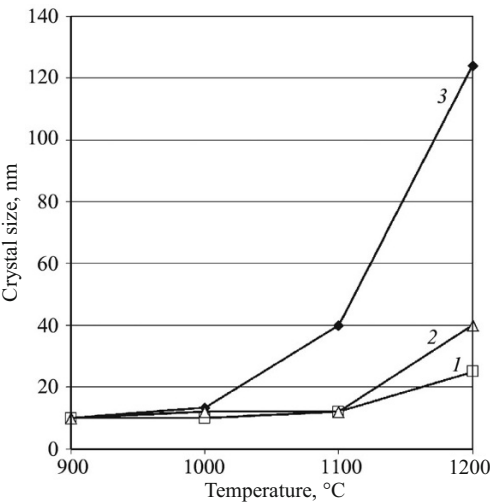


Fig. 3. Sizes of AMS-2 crystals versus the heat-treatment temperature: 1) undoped sample; 2) sample with LiF; 3) sample with B₂O₃.

acid. Analysis of the data in Figs. 1 and 2 shows that the heat-treatment of the AMS-2 powder at 900°C does not appreciably change the particle size. At the same time, after heat treatment at 1100°C the average particle size increases to 70 nm. We also note that no nonuniformities are observed in the structure of the additive containing materials which we formed (Figs. 1*b* and 2).

Curves of the sizes of spinel crystals versus the heat-treatment temperature in the initial AMS-2 powder (curve 1) as well as in powder with sintering additives LiF (curve 2) and B₂O₃ (curve 3) are displayed in Fig. 3. It is clearly seen that the additions of lithium fluoride and boric acid in the amounts 1% (mass fraction) significantly accelerates the growth of spinel crystals, which is clearly manifested at temperatures above 1000°C. The experimental data presented attest that a nanosize coating obtained as a result of the action of boric acid accelerates the growth of spinel crystal during heat treatment more than the sintering additive lithium fluoride.

Measurements of the average (10 samples were measured in each series) values of the density of sample obtained

by cold pressing with drying at temperature 100°C and sintering in air at 1200°C are presented in Table 1. The experimental data presented show that, in the case where the AMS-2 powder was cold-pressed the addition of water yields somewhat denser samples than those obtained using the other liquids.

The effect of adding boric acid on the density of samples obtained during heat treatment manifests much more clearly. The samples obtained in this case acquire density much more quickly (see Table 1).

The values of the relative density of the AMS-1 and -2 ceramic samples sintered in air at 1300°C in 6 h are presented in Table 2. These samples were obtained by permeating porous samples with alcohol solutions of boric acid with different concentrations. The introduction of boric acid significantly accelerates the sintering of the samples fabricated from micron-size spinel powders (AMS-1), and this effect intensifies with increasing concentration of the permeating solution (see Table 2). The investigation of the AMS-2 samples formed from nanosize powder showed that their relative density does not depend on the concentration of the boric acid introduced into the permeating solution. This could be associated with the fact that these samples, sintered at 1250°C, acquired high relative density of 79% even before permeation, and any further increase in the density during sintering is not as obvious as in the samples obtained from AMS-1 powder.

Comparing the experimental data presented in Table 1 also shows that for similar technological conditions the use of nanosize powders as precursors makes it possible to increase the density of the ceramic samples by 10 – 15%.

In summary, it can be concluded that treating with alcohol solutions of boric acid both powder aluminum-magnesium spinel and monolithic porous samples fabricated from it results in high rates of buildup of the relative density of the ceramic.

SEM photographs of the inner layers and surface of the AMS-2 ceramic sample, obtained by sintering without the addition of sintering additive for 120 min at 1200°C, are displayed in Fig. 4. Comparing the data presented in Fig. 4 shows a considerable difference in the structure of the inner and outer layers of the ceramic.

TABLE 1. Relative Density ρ/ρ_{theor} Samples Obtained by Cold Pressing with Additions of Different Liquids

Additive	Relative density ρ/ρ_{theor} , %			
	Drying at 100°C	Sintering at 1200°C in air, min		
		1	60	600
No additives (dry pressing)	37	69	80	82
Water	41	71	82	86
Ethanol	38	71	82	83
Solution of boric acid in ethanol	38	83	88	89

TABLE 2. Relative Density ρ/ρ_{theor} of the Samples Fabricated from AMS-1 and AMS-2 Powders Unpermeated (for Comparison) and Permeated with Alcohol Solutions of Boric Acid, after Sintering for 6 h at 1300°C

Boric acid mass fraction in solution, %	ρ/ρ_{theor} , %	
	AMS-1	AMS-2
3.1	78	94
2.3	87	86
1.5	85	89
0.8	79	93
0	56	90

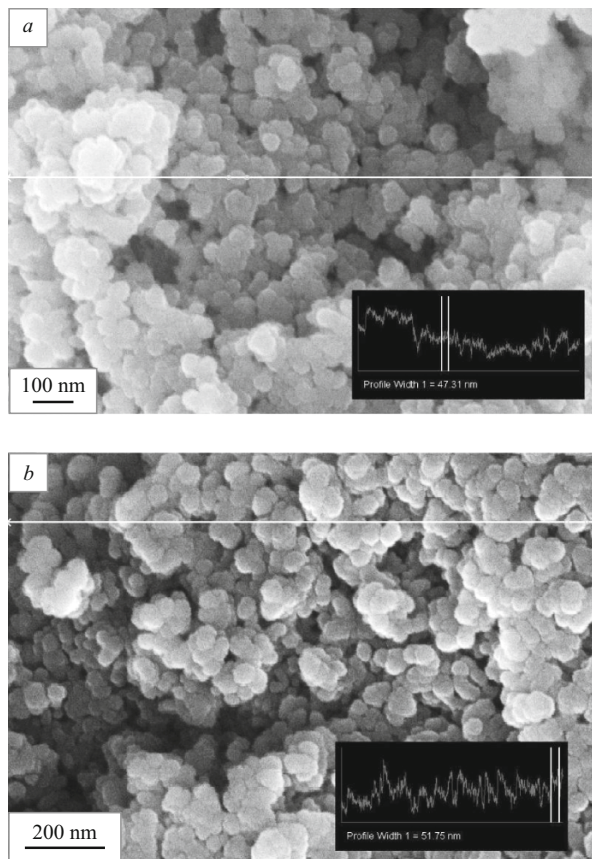


Fig. 4. SEM photographs of the ceramic sample AMS-2 heat-treated at 1200°C for 120 min: a) inner layers; b) outer surface.

The inner layers of the ceramic sample consist of AMS particles with quite uniform sizes (average size 180 nm). Comparing the data presented in Figs. 1a, 2a and 4a shows that during heat-treatment of the material the spinel particles become considerably larger while retaining their rounded shape.

The photomicrograph of the surface layer touching the die during formation attests that quite large ($> 1 \mu\text{m}$) aggregates consisting of close-packed particles form in this layer. The size of these particles is close to that of the particles in the inner layers of the sample. From a comparison of the particle sizes of the samples in Fig. 4a and b it becomes obvious that the particles in the surface layer sintered during heat-treatment much more efficiently than in the inner layers of the sample and the relative density of the surface layer of the sample increased. It is known [6, pp. 75 – 96] that differences in the porosity of the surface and inner layers of the material can form in samples obtained by cold uniaxial pressing of powders. These differences in the porosity and structure of the materials increase with increasing ratio of the thickness h of layer of pressed powder to the hydraulic radius

R_h of the layer. The data on the difference in the density inside the samples obtained by uniaxial pressing of fireclay powder which are presented in [6, pp. 81 – 85] attest that its magnitude can reach 10% or more.

The difference in the morphological features of the surface and inner layers of the sample as observed by comparing the data presented in Fig. 4a and b can be attributed to the formation of a nonuniform stress field at the stage of cold-pressing of the powdered samples. The structural features of the surface and inner layers of the pressed samples must be taken into account in the high-temperature process in order to reach the maximum density of ceramic articles and, specifically, to obtain an optical ceramic based on nanopowders of aluminum-magnesium spinel.

CONCLUSIONS

1. The deposition, by the method developed, of an H_3BO_3 coating of an alcohol solution on the surface of AMS particles makes it possible to create a nanosize coating consisting of B_2O_3 on the surface of the spinel particles during subsequent heat-treatment.
2. Compared with undoped and LiF-doped AMS samples the sintering of AMS nanopowders, whose particles have a nanosize B_2O_3 coating, occurs with accelerated growth of the aluminum-magnesium spinel grains, which permits obtaining a high-density ceramic.
3. The AMS samples studied can be arranged in the following order according to how effectively the form of the sintering additive affects the average grain size: AMS (undoped sample) \rightarrow AMS + LiF \rightarrow AMS + B_2O_3 .

REFERENCES

1. G. I. Belykh, V. T. Gritsyna, and L. V. Udalova, "Structural and mechanical properties of optical ceramic obtained from magnesium-aluminum spinel," *Vopr. Atom. Nauki Tekh.*, **85**(3), 101 – 107 (2004).
2. J. Qi, T. Lu, X. Chang, and M. Lei, "Preparation of $MgAl_2O_4$ transparent nano-ceramics and their light transmission properties," *Key Eng. Mater.*, **336 – 338**, 2296 – 2299 (2007).
3. R. O. Loutfy, J. L. Sepulveda, and S. Chang, "Ready-to-sinter spinel nanomixture and method for preparing same," US Patent Application US 2010/0056357 A1 (04.03.2010); C04B35/04; C04B35/043; C04B35/64.
4. N. Frage, M. Dariel, S. Meir, and S. Kalabuchov, "Single-stage thermal process for manufacturing transparent sintered spinel," US Patent Application US 2009/297851 A1 (03.12.2009); B32B5/16; C01F7/16; B32B5/16; C01F7/00.
5. K. Tsukuma, "Transparent $MgAl_2O_4$ spinel ceramics produced by HIP post-sintering," *J. Ceram. Soc. Jpn.*, **114**(10), 802 – 806 (2006).
6. R. Ya. Popil'skii and Yu. E. Pivinskii, *Pressing of Powder Ceramic Bodies* [in Russian], Metallurgiya, Moscow (1983).